

Consequences for Exchange Energy Density Functional of Exponentially Decaying Nature of Atomic Electron Densities

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ABSTRACT: A simple model is studied for the atomic exchange energy density functional, which is based on the exponential decaying feature of the density and the Fermi–Amaldi model for exchange correlation. The model is exact for hydrogen-like atoms. It is shown to provide a reasonable approximation for many-electron atoms. The local exchange energy density and potential are expressed as universal functions of \mathbf{r} , $\rho(\mathbf{r})$, and $|\nabla\rho(\mathbf{r})|$, and go beyond the generalized gradient approximation (GGA) framework in which $E_x[\rho] = \int e_x(\rho, \nabla\rho) d\mathbf{r}$. The conclusion reached previously by Gill and Pople (*Phys. Rev. A* 1993, 47, 2383), that the general atomic exchange functional cannot be of the GGA form, is supplemented by the more optimistic conclusion that it could well have the form $E_x[\rho] = \int e_x(\mathbf{r}, \rho, \nabla\rho) d\mathbf{r}$. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 2–11, 1999

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Introduction

Density functional theory (DFT) has been proven computationally efficient, conceptually insightful, and generally useful in recent years.^{1–5} Its intrinsic problem of the unknown form of the universal energy density functional, $F[\rho]$, however, prevents us from performing accurate *ab initio* DFT calculations. Exchange and exchange correlation are principal parts of this problem. Exchange-correlation potentials calculated from the gradient expansion approximation (GEA), or the generalized gradient approximation (GGA),^{6,7} are found to be not very well-behaved.⁸

Recently, Gill and Pople⁹ have shown that the accurate exchange energy of many-electron atoms cannot have the GGA form:

$$E_s[\rho] = \int e_x(\rho, \nabla\rho) d\mathbf{r} \quad (1)$$

In the present study, we reach a more positive conclusion that the form, beyond GGA:

$$E_x[\rho] = \int e_x(\mathbf{r}, \rho, \nabla\rho) d\mathbf{r} \quad (2)$$

may well be highly accurate or exact for the many-electron atom.

Starting from the exponential decaying nature of the atomic electron density, we here attempt to extract major features of the exchange energy density functional for atoms. The model proposed is exact for the hydrogen-like system, and it also provides useful semiquantitative results for the many-electron atomic systems. We find that, within our model, a proper description of the exchange energy density functional demands going beyond the GEA/GGA framework. The exchange potential found is well-behaved. Numerical tests are carried out for first- and second-row atoms, giving reasonable (although not accurate) values of exchange and conforming to known qualitative behavior of exchange potentials.

Models for Atomic Density and Exchange Energy Functional

Let us suppose that the electron density, $\rho(\mathbf{r})$, of atoms is a simple exponential function of the distance:

$$\rho(\mathbf{r}) \sim e^{-2\zeta r} \quad (3)$$

where the effective nuclear charge, ζ , is a constant. The normalization condition of the density requires that:

$$\int \rho(\mathbf{r}) d\mathbf{r} = N \quad (4)$$

where N is the total number of electrons of the system concerned. Eqs. (3) and (4) give a normalized density of the form:

$$\rho(\mathbf{r}) = N \left(\frac{\zeta^3}{\pi} \right) e^{-2\zeta r} \quad (5)$$

This form of electron density differs markedly from that of the homogeneous electron gas in that:

$$\frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})} = \text{const} = 2\zeta \quad (6)$$

Consequently:

$$\rho(\mathbf{r}) = \frac{N}{\pi} \left(\frac{|\nabla\rho(\mathbf{r})|}{2\rho(\mathbf{r})} \right)^3 e^{-r|\nabla\rho(\mathbf{r})|/\rho(\mathbf{r})} \quad (7)$$

Note that this relation between the density and its gradient is system independent. We may regard eq. (7) as a simple, although approximate, embodiment of the exponential character of atomic densities. It is exact for the hydrogen-like atom.

Consider now the exchange-energy functional $E_x[\rho]$. We take the Fermi–Amaldi model,¹⁰ known to be fairly good,^{11–14} in which $E_x[\rho]$ is approximated by the classical Coulomb repulsion via:

$$E_x[\rho] = -\frac{J[\rho]}{N} \quad (8)$$

where:

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (9)$$

The exchange potential associated with eq. (8) is:

$$v_x(\mathbf{r}) = \frac{\delta E_x[\rho]}{\delta\rho(\mathbf{r})} = -\frac{v_f(\mathbf{r})}{N} \quad (10)$$

where:

$$v_f(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (11)$$

In deriving eq. (8), N has been kept fixed, as customarily done in the Kohn–Sham formulation.

If one allows N to change, a constant term J/N^2 would appear in the potential. These formulas are exact for the hydrogen-like atom.

Inserting eq. (5) into eq. (10), and using eq. (6), we find a universal (although, in general, approximate) density functional for the exchange potential:

$$v_x(\mathbf{r}) = -\frac{1 - \exp\left[-r \frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})}\right]}{r} + \frac{|\nabla\rho(\mathbf{r})|}{2\rho(\mathbf{r})} \exp\left[-r \frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})}\right] \quad (12)$$

while the exchange energy density functional of eq. (8) becomes:

$$E_x[\rho] = -\frac{1}{2} \int \rho(\mathbf{r}) \left\{ \frac{1 - \exp\left[-r \frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})}\right]}{r} - \frac{|\nabla\rho(\mathbf{r})|}{2\rho(\mathbf{r})} \exp\left[-r \frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})}\right] \right\} d\mathbf{r} \quad (13)$$

Eq. (13) may be found in a study by Berrondo and Goscinski.^{15,16} These investigators began with the assumption that the first-order density matrix takes a real exponential form, and then imposed the idempotency condition on the density matrix to arrive at eq. (13).

There is another formula for calculating E_x when the exchange potential is known, the Levy-Perdew relation¹⁷:

$$E_x[\rho] = -\int \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_x(\mathbf{r}) d\mathbf{r} \equiv \int [3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla\rho(\mathbf{r})] v_x(\mathbf{r}) d\mathbf{r} \quad (14)$$

If v_x and ρ are known exactly, eqs. (13) and (14) must give the same value for E_x .

GGA, $E_x[\rho]$ has the form:

$$E_x[\rho] = \int e_x(\rho(r), |\nabla\rho(r)|) d\mathbf{r} \quad (15)$$

whereas, in eq. (13), one has:

$$E_x[\rho] = \int e_x(\mathbf{r}, \rho(r), |\nabla\rho(r)|) d\mathbf{r} \quad (16)$$

which is a generalization¹⁸ of GGA and the weighted density approximation (WDA).¹⁹ For atoms, the origin for \mathbf{r} is the atomic nucleus, and the occurrence of \mathbf{r} in the functional does not detract from its universality, because the location of the nucleus is at the density maximum, and therefore a functional of the density.

2. $E_x[\rho]$ in eq. (13) involves the first power of the density gradient. [To confirm this, assume $\nabla\rho/\rho$ is small and expand the integrand in eq. (13).] This term in the gradient is not allowed in the classical gradient expansion formalism. Note that there are earlier suggestions²⁰⁻²² that first-order gradient terms be included for atoms and molecules.
3. Unlike the usual GGA potentials,⁸ eq. (12) is well-behaved at both the nuclear cusp and at long range. It has a finite value of $-Z$ at the nuclear cusp,²³ and decays like $-1/r$ when r becomes large.
4. The $E_x[\rho]$ formula in eq. (13) is a homogeneous functional of degree 1 with respect to density scaling; that is²⁴:

$$\int \rho(\mathbf{r}) \frac{\delta E_x[\rho]}{\delta \rho(\mathbf{r})} d\mathbf{r} = E_x[\rho] \quad (17)$$

Note that the quantity $\{\exp[-r(|\nabla\rho(r)|/\rho(r))]\}$ is invariant to both density scaling and coordinate scaling. The behavior of eq. (13) with respect to density scaling accords with a recent argument that the universal form of $V_{ee}[\rho]$ may be written as a combination of density homogeneous functionals of degree 1 and 2.²⁵

Hydrogen-Like Systems

For a hydrogen-like system, the exact wave function and density are:

$$\Psi(r) = \sqrt{\frac{Z^3}{\pi}} \exp(-Zr) \quad (18)$$

Features of Model Functional and Potential

1. $E_x[\rho]$ goes beyond the generalized gradient approximation (GGA) framework. In any

and:

$$\rho(r) = \frac{Z^3}{\pi} \exp(-2Zr) \quad (19)$$

where Z is the nuclear charge. There are no dynamic correlation effects; that is, $E_c[\rho] = T_c[\rho] = 0$, and therefore the exchange energy must precisely cancel the classical Coulomb repulsion energy. So, eqs. (5) and (8) are exact for this type of system. Hence, the exact exchange energy quantities for the hydrogen-like system satisfy eqs. (12) and (13). A formal proof of these two equations in the manner of Berrondo and Goscinski¹⁵ is given in Appendix 1.

Within the GGA framework of eq. (1), Gill and Pople recently⁹ derived a formula for the exchange energy functional for the hydrogen-like system. Specifically, they assumed that the exchange energy density is a function of only ρ and the dimensionless quantity, $x = |\nabla\rho|/\rho^{4/3}$; that is:

$$E_x[\rho] = \int \rho^{4/3}(\mathbf{r}) g(x) d\mathbf{r} \quad (20)$$

They then proved that there was one and only one well-behaved $g(x)$ such that both this formula and the exact formula for hydrogen-like systems:

$$\begin{aligned} v_x(\mathbf{r}) &= -v_j(\mathbf{r}) \\ &= \frac{1 - \exp(-2Zr)}{r} + Z \exp(-2Zr) \end{aligned} \quad (21)$$

hold exactly. Then testing the resultant eq. (20) for many-electron atoms, they found poor results, proving conclusively that eq. (20) is unacceptable as a universal form for $E_x[\rho]$.

Now, requiring eq. (12), as we have done, is different from requiring eq. (20). Again the hydrogen-like system is included as a special case, but

the corresponding density functional, eqs. (12) and (13), are different, universal, but approximate functionals for non-hydrogen-like systems. The form goes beyond GGA, being:

$$E_x[\rho] = \int \rho^{4/3}(\mathbf{r}) g(r, x) d\mathbf{r} \quad (22)$$

We propose eqs. (12) and (13) as acceptable accurate descriptions of hydrogen-like systems. The fact that Gill and Pople have found a unique GGA $g(x)$ for eq. (20) does not preclude eq. (22) from also being accurate, or the non-GGA eq. (13).

To summarize, in the present eqs. (12) and (13), and in Gill and Pople's formalism, the exact density of the hydrogen-like system has been employed in different ways. This means that the exchange energy functional and the exchange potential derived from these formulations are not, in general, valid for any trial density. The universal forms of the exchange energy functional and its potential for the one-electron system should be the non-GGA $E_{xc} = -J$ and $v_{xc} = -v_j$. However, as we show in Appendix 2, with the formulas we have obtained, as well as those of Gill and Pople, one still gets the exact density at the solution point for the hydrogenic system.

To confirm numerically the aptness of our description of the one-electron atomic system, we perform self-consistent-field (SCF) calculations for a few hydrogen-like species via the one-electron Kohn-Sham equation,²⁶ simply:

$$\left\{ -\frac{1}{2}\nabla^2 - \frac{Z}{r} + \int \frac{\rho(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_x(r) \right\} \phi = \varepsilon \phi$$

with $\rho(r) = |\phi|^2$ (24)

where $v_x(r)$ is given by eq. (12). No exact wave functions are put into the calculations. Table I exhibits the SCF results obtained. The total energy

TABLE I.
Self-Consistent-Field Results from Kohn-Sham Equation for Some One-Electron Atomic Systems.^a

	Exchange energy		Total energy	
	Exact	Present SCF	Exact	Present SCF
H	-0.3125	-0.3125	-0.5000	-0.5000
He ⁺	-0.6250	-0.6250	-2.0000	-1.9999
Be ⁺³	-1.2500	-1.2499	-8.0000	-7.9995
C ⁺⁵	-1.8750	-1.8749	-18.000	-17.999
Ne ⁺⁹	-3.1250	-3.1249	-50.000	-49.999
Ar ⁺¹⁷	-5.6250	-5.6248	-162.00	-161.98

^aThe exchange-correlation potential is from eq. (12).

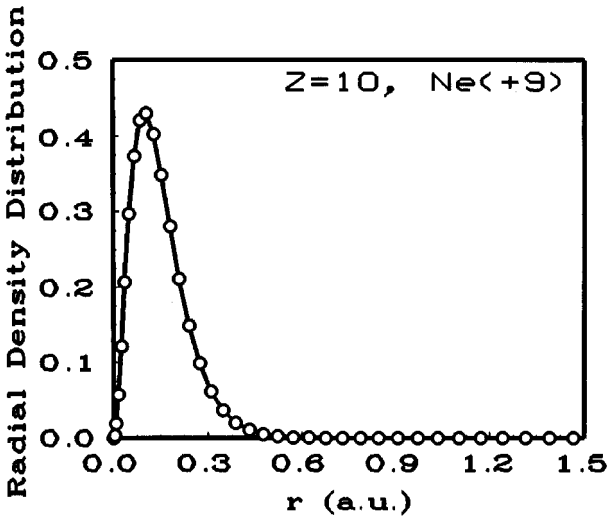


FIGURE 1. Exact (solid line) and calculated self-consistent-field (scattered in symbol “o”) radial density distribution functions of Ne^{+9} ion.

and the exchange energy are reproduced exactly, even though eq. (24) is not the conventional Schrödinger equation for hydrogen-like species. Figure 1 shows the exact and calculated SCF radial density distribution functions for the Ne^{+9} species. They agree.

Many-Electron Atomic Systems

We now turn to the model many-electron atom, in which the electron density is exponentially decaying. (Better, would be a model in which the density is piecewise exponentially decaying, a good approximation that was discussed in ref. 27. Although we have not treated the piecewise-exponential model in any detail, we believe that it generally must lead to forms falling outside the GEA/GGA framework.)

We have performed some sample calculations on many-electron atomic systems, assuming that eqs. (12), (13), and sometimes eq. (14) are valid. Quantities investigated include the local exchange energy density, total exchange energy, exchange potential, and self-consistent-field density. The Hartree–Fock densities of Clementi and Roetti²⁸ were employed.

Tables II–IV list the exact Hartree–Fock and approximate exchange energies calculated from eq. (13) for various light atoms and ions. Table II displays the results for neutral atoms from H to Ar, compared with those from the Dirac form, and the virial relation, eq. (14). We find that, for H,

TABLE II.
Exact Hartree–Fock and Approximate Exchange Energies for First- and Second-Row Atoms.^a

Atom	Dirac	Eq. (13)	Eq. (14) ^b	Exact
H	−0.213	−0.313	−0.313	−0.313
He	−0.88	−1.07	−1.17	−1.03
Li	−1.52	−1.82	−1.99	−1.78
Be	−2.31	−2.68	−2.96	−2.67
B	−3.26	−3.65	−4.19	−3.74
C	−4.40	−4.74	−5.66	−5.05
N	−5.75	−5.95	−7.34	−6.60
O	−7.28	−7.26	−9.20	−8.17
F	−9.04	−8.68	−11.25	−10.00
Ne	−11.03	−10.21	−13.46	−12.11
Na	−12.77	−11.65	−15.50	−14.02
Mg	−14.61	−13.15	−17.66	−15.99
S	−22.96	−19.57	−26.88	−25.00
Ar	−27.86	−23.07	−31.85	−30.19

^a Approximate formulas used are the Dirac local form and Eq. (13).

^b Virial relation from the approximated $v_x(r)$, Eq. (14).

both equations reproduce the exact value. For atoms He to Be, the results calculated from eq. (13) are somewhat larger than the exact, whereas for the rest they are smaller with the difference increasing as the atomic number increases. The Dirac formula gives smaller values than eq. (13) for small atoms, but larger after oxygen. Eq. (14) always yields values larger than the exact. In Tables

TABLE III.
Exact Hartree–Fock and Approximate Exchange Energies for He Isoelectronic Atomic Ions, Compared with Results from Dirac Form.

Ion	Dirac	Eq. (13)	Exact
Li ⁺	−1.42	−1.69	−1.65
Be ⁺²	−1.96	−2.32	−2.28
B ⁺³	−2.49	−2.94	−2.90
C ⁺⁴	−3.03	−3.57	−3.53
N ⁺⁵	−3.57	−4.19	−4.15
O ⁺⁶	−4.10	−4.82	−4.78
F ⁺⁷	−4.64	−5.44	−5.40
Ne ⁺⁸	−5.17	−6.07	−6.03
Na ⁺⁹	−5.71	−6.69	−6.65
Mg ⁺¹⁰	−6.25	−7.32	−7.28
Al ⁺¹¹	−6.78	−7.94	−7.90
Si ⁺¹²	−7.32	−8.57	−8.53
P ⁺¹³	−7.85	−9.19	−9.15
S ⁺¹⁴	−8.39	−9.82	−9.78
Cl ⁺¹⁵	−8.91	−10.44	−10.40
Ar ⁺¹⁶	−9.46	−11.07	−11.03

TABLE IV.
Exact Hartree–Fock and Approximate Exchange
Energies for Be Isoelectronic Atomic Ions, Compared
with Results from Dirac Form.

Ion	Dirac	Eq. (13)	Exact
B^+	−3.04	−3.48	−3.49
C^{+2}	−3.76	−4.28	−4.31
N^{+3}	−4.48	−5.07	−5.14
O^{+4}	−5.20	−5.87	−5.96
F^{+5}	−5.92	−6.67	−6.78
Ne^{+6}	−6.63	−7.46	−7.60
Na^{+7}	−7.35	−8.26	−8.42
Mg^{+8}	−8.07	−9.06	−9.24
Al^{+9}	−8.79	−9.85	−10.05
Si^{+10}	−9.51	−10.65	−10.87
P^{+11}	−10.23	−11.44	−11.69
S^{+12}	−10.95	−12.24	−12.51
Cl^{+13}	−11.66	−13.04	−13.33
Ar^{+14}	−12.38	−13.83	−14.15

III and IV, results are shown for the He and Be isoelectronic species, respectively. Values from eq. (13) agree well with exact values.

Plots of the local exchange energy density are given in Figure 2 for He and Figure 3 for Be. Figure 2 shows that our model, eq. (13), produces results for He accurate except for a small deviation near the nuclear cusp. From Figure 3, one sees that the values within each of the two atomic shells have been well reproduced; there is an error only in the region between these shells.

To illustrate how eq. (12) is a reasonable simulation of the correct exchange potential $v_x(r)$, Figures 4–6 show the exact^{29,30} and approximate $v_x(r)$ for the atoms He, Ne, and Ar. Three important

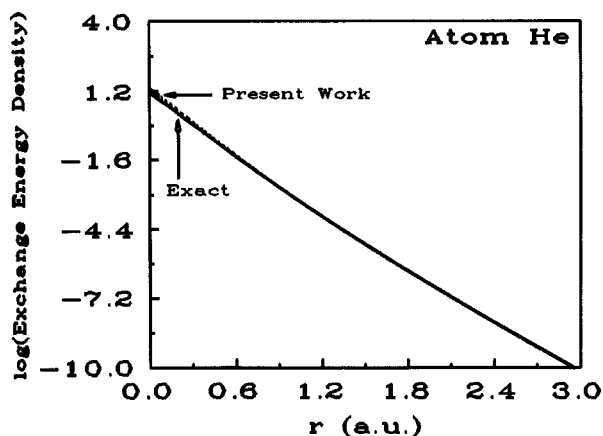


FIGURE 2. Exact (solid line) and approximate (dashed line) local exchange energy density functions of He.

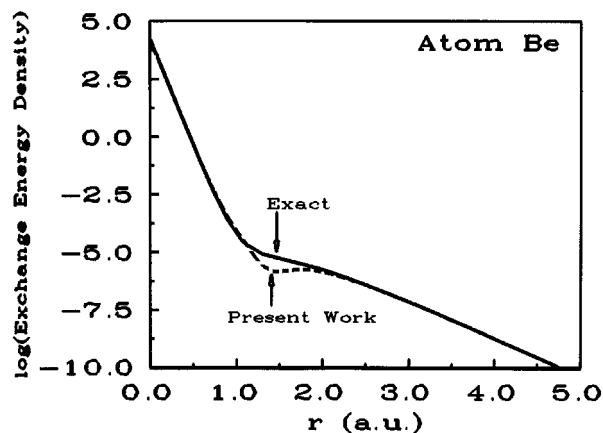


FIGURE 3. Exact (solid line) and approximate (dashed line) local exchange energy density functions of Be.

features are observed: (i) At the nuclear cusp, both v_x values are finite. This contrasts with the well-known divergence problem of conventional GEA/GGA potentials near nuclear cusps. Eq. (12) gives a value of $-Z$ for $v_x(0)$. The exact $v_x(0)$ is generally somewhat larger than this value. (ii) Asymptotically, the simulated v_x (the dashed line) goes correctly as $-1/r$ as the exact potential (the solid line). This feature predicts that using eq. (12) to perform Kohn–Sham calculations would result in a reasonable highest occupied orbital energy even with neglect of the E_c contribution. (iii) Shell structures are correctly reproduced. The model and exact v_x curves have similar shapes. Notice, however, in Table II, the correct exchange energy values have not been well reproduced for Ne and Ar

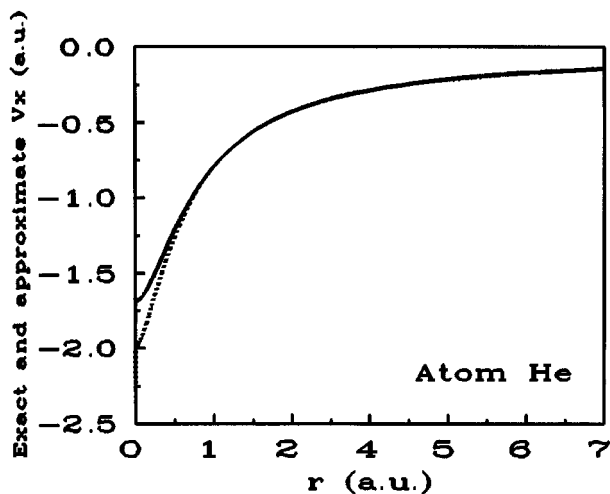


FIGURE 4. Exact (solid line) and approximate (dashed line) exchange potential $v_x(r)$ of He.

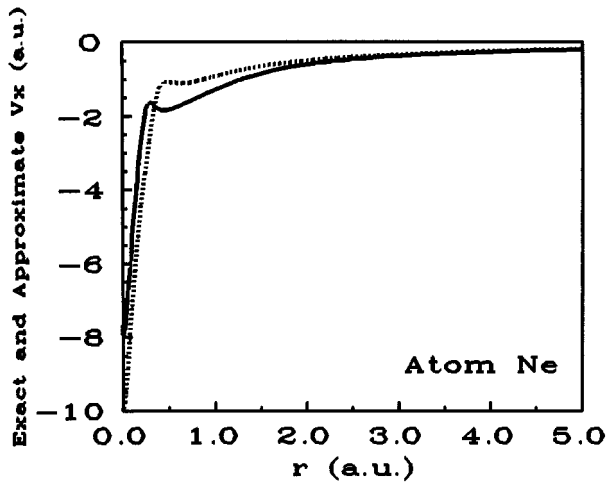


FIGURE 5. Exact (solid line) and approximate (dashed line) exchange potential $v_x(r)$ of Ne.

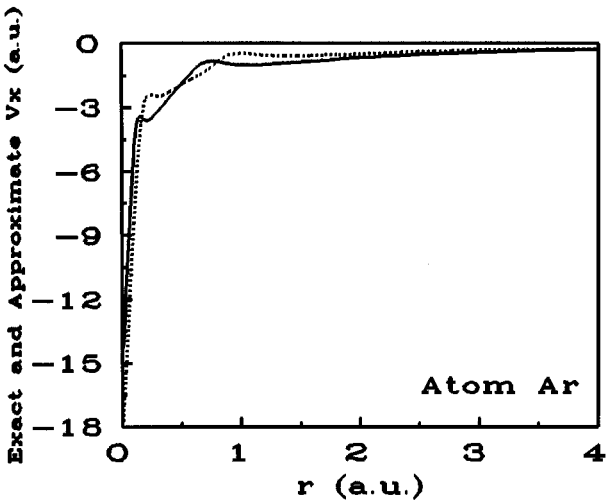


FIGURE 6. Exact (solid line) and approximate (dashed line) exchange potential $v_x(r)$ of Ar.

atoms, although their v_x curves seem well behaved. The errors come from the medium range of r , where we lack accurate description.

With use of the approximate $v_x(r)$, self-consistent-field calculations have been performed for first- and second-row atoms. Table V shows the E_x and total energy values obtained from these SCF calculations. The accurate exchange and total energy values are from the optimized potential model (OPM).^{31, 32} Also given in this table are the exact and calculated highest occupied orbital energies (see ref. 1 for the proof that $\epsilon_{\text{HOMO}} = -I$). Contri-

butions from the E_c component have not been taken into account. The results are reasonable. In Figures 7 and 8, the SCF radial density functions of Be and Ne are plotted, along with the exact Hartree-Fock results. Excellent agreement is seen for Be, but only semiquantitative agreement is found for Ne. We conclude that eqs. (12) and (13) are decent approximate formulas for many-electron atoms. This supports our belief that very accurate approximations of the form of eq. (16) ultimately may be found.

TABLE V. Exact and Approximate Results of Exchange Energy (E_x), Total Energy (E_{tot}), and Highest Occupied Orbital Energy (HOMO) from Self-Consistent-Field Calculations for First- and Second-Row Atoms.

Atom	Exchange energy		Total energy		HOMO calc.	-I exact
	Calc.	OPM ^a	Calc.	OPM ^{a, b}		
He	-1.09	-1.03	-2.80	-2.86	-0.95	-0.90
Li	-1.87	-1.78	-7.32	-7.43	-0.21	-0.20
Be	-2.73	-2.67	-14.53	-14.57	-0.32	-0.34
B	-3.73	-3.74	-24.46	-24.53	-0.27	-0.31
C	-4.84	-5.05	-37.49	-37.69	-0.34	-0.41
N	-6.05	-6.60	-53.91	-54.40	-0.41	-0.53
O	-7.37	-8.17	-74.02	-74.81	-0.48	-0.50
F	-8.79	-10.00	-98.10	-99.41	-0.56	-0.64
Ne	-10.74	-12.11	-126.5	-128.6	-0.65	-0.79
Na	-11.78	-14.02	-158.8	-161.9	-0.21	-0.19
Mg	-13.29	-15.99	-195.9	-199.6	-0.27	-0.28
S	-19.70	-25.00	-392.1	-397.5	-0.33	-0.38
Ar	-23.19	-30.19	-520.7	-526.8	-0.44	-0.58

^a Ref. 31. ^b Ref. 32.

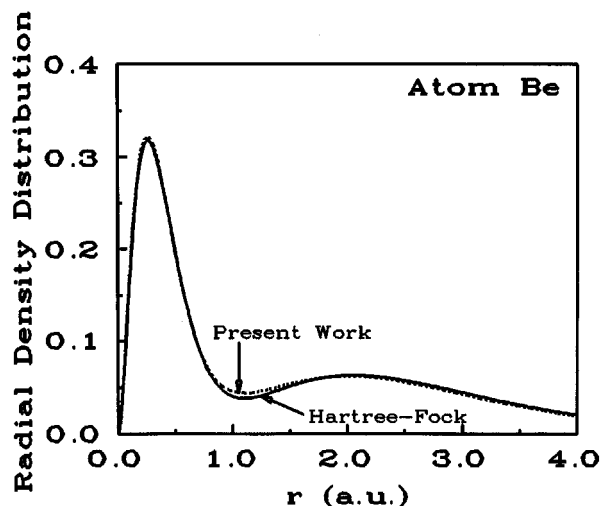


FIGURE 7. Exact (solid line) and approximate (dashed line) self-consistent-field radial density distribution functions of Be.

Summary

The density functional formulation of the exchange energy and exchange potential for the hydrogen-like system and an extension of it to many-electron atomic systems have been discussed in this work. Given the awkwardness of the GGA solution found by Gill and Pople, and its failure when extended to many-electron atoms,⁹ we conclude that, in the hydrogen-like system, the

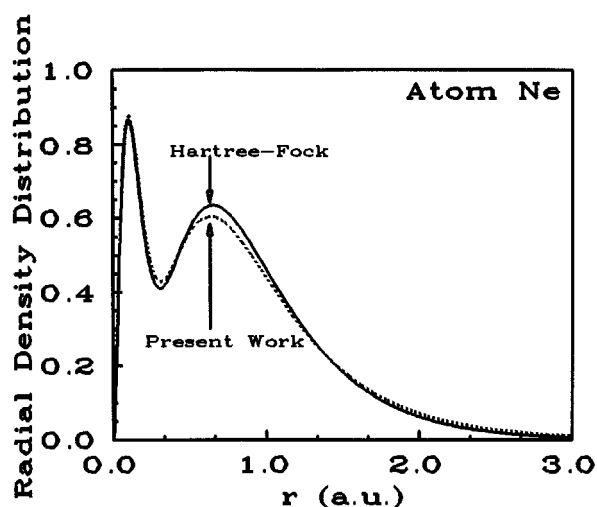


FIGURE 8. Exact (solid line) and approximate (dashed line) self-consistent-field radial density distribution functions of Ne.

exchange energy and exchange potential are best expressible beyond the GGA framework. In their article, Gill and Pople state that their analysis “reflects the great disparity between the uniform gas and the hydrogen atom.” We agree about the disparity. Exponential fall-offs from atomic nuclei characterize the electron densities of all atoms and molecules. Their electron densities are far from uniform electron distributions.

Appendix 1: Formal Proof of Eqs. (12) and (13)

The normalized density of the hydrogen-like system is:

$$\rho(r) = \frac{\zeta^3}{\pi} \exp(-2\zeta r) \quad (\text{A1})$$

with constant $\zeta = |\nabla\rho|/2\rho$. The first-order reduced density matrix accordingly is:

$$\begin{aligned} \gamma_1(r, r') &= \Psi(r)\Psi(r') = \rho^{1/2}(r)\rho^{1/2}(r') \\ &= \frac{\zeta^3}{\pi} \exp[-\zeta(r + r')] \end{aligned} \quad (\text{A2})$$

This form satisfies the idempotency condition:

$$\int \gamma_1(r, r'')\gamma_1(r'', r') dr'' = \gamma_1(r, r') \quad (\text{A3})$$

and the requirement

$$\gamma_1(r, r')|_{r=r'} = \rho(r) \quad (\text{A4})$$

This form of the first-order density matrix yields the exchange charge:

$$\rho_x(r, r') = -\frac{|\gamma_1(r, r')|^2}{\rho(r)} = -\frac{\zeta^3}{\pi} \exp(-2\zeta r') \quad (\text{A5})$$

and the pair distribution function:

$$h_x(r, r') = -\frac{\gamma_1(r, r')\gamma_1(r', r)}{\rho(r)\rho(r')} = -1 \quad (\text{A6})$$

These exchange charge and pair distribution functions satisfy the normalization conditions:

$$\int \rho_x(r, r') dr' = \int \rho(r')h_x(r, r') dr' = -1 \quad (\text{A7})$$

To get the total exchange energy functional, one uses:

$$E_x[\rho] = \frac{1}{2} \int \rho(r) V_s(r) d\mathbf{r} \quad (\text{A8})$$

where the Slater potential is defined as:

$$V_s(r) = \int \frac{\rho_x(r, r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (\text{A9})$$

Meanwhile, the exchange potential $v_x(r)$ relates to the Slater potential via:

$$\begin{aligned} v_x(r) &= \frac{\delta E_x[\rho]}{\delta \rho(r)} = V_s(r) \\ &+ \frac{1}{2} \iint \frac{\rho(r') \rho(r'')}{|\mathbf{r}' - \mathbf{r}''|} \frac{\delta h_x(r', r'')}{\delta \rho(\mathbf{r})} d\mathbf{r}' d\mathbf{r}'' \end{aligned} \quad (\text{A10})$$

Insert eq. (A5) in eq. (A9), and using eq. (8), one obtains eq. (13) of the text. From eqs. (A6) and (A10), one obtains eq. (12) of the text.

Appendix 2: Uniqueness of Solution for Hydrogen-Like System

The Schrödinger equation of the hydrogen-like system is:

$$\left[-\frac{1}{2} \nabla^2 - \frac{Z}{r} \right] \Psi_0 = E_0 \Psi_0 \quad (\text{A11})$$

and the Kohn–Sham equation of the system is:

$$\left[-\frac{1}{2} \nabla^2 - \frac{Z}{r} + v_J + v_{xc} \right] \Psi = E \Psi \quad (\text{A12})$$

where:

$$v_J = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (\text{A13})$$

and:

$$v_{xc} = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \quad (\text{A14})$$

The densities from the two schemes are ρ_0 and ρ , respectively:

$$\rho_0 = |\Psi_0|^2 \quad (\text{A15})$$

and:

$$\rho = |\Psi|^2 \quad (\text{A16})$$

Now, we prove that by v_{xc} taking eq. (12), eq. (A12) gives the same density as eq. (A11); that is, $\rho_0 = \rho$.

Assume that eqs. (A11) and (A12) give different wave functions and thus different densities. The total energies calculated from these two equations are then:

$$E_0 = \langle \Psi_0 | -\frac{1}{2} \nabla^2 - \frac{Z}{r} | \Psi_0 \rangle \quad (\text{A17})$$

and:

$$E = \langle \Psi | -\frac{1}{2} \nabla^2 - \frac{Z}{r} + v_J + v_{xc} | \Psi \rangle \quad (\text{A18})$$

According to the variational principle of these two equations, one obtains:

$$\begin{aligned} E &= \langle \Psi | -\frac{1}{2} \nabla^2 - \frac{Z}{r} | \Psi \rangle + \langle \Psi | v_J + v_{xc} | \Psi \rangle \\ &\geq E_0 + \langle \Psi | v_J + v_{xc} | \Psi \rangle \end{aligned} \quad (\text{A19})$$

and:

$$\begin{aligned} E_0 &= \langle \Psi_0 | -\frac{1}{2} \nabla^2 - \frac{Z}{r} + v_J + v_{xc} | \Psi_0 \rangle \\ &+ \langle \Psi_0 | v_{xc} - v_J | \Psi_0 \rangle \\ &\geq E + \langle \Psi_0 | v_{xc} - v_J | \Psi_0 \rangle \end{aligned} \quad (\text{A20})$$

Adding eqs. (A19) and (A20), one has:

$$\begin{aligned} E_0 + E &\geq E + E_0 + \langle \Psi_0 | v_{xc} - v_J | \Psi_0 \rangle \\ &+ \langle \Psi | v_J - v_{xc} | \Psi \rangle \end{aligned} \quad (\text{A21})$$

Or:

$$\langle \Psi_0 | v_{xc} - v_J | \Psi_0 \rangle + \langle \Psi | v_J - v_{xc} | \Psi \rangle \leq 0 \quad (\text{A22})$$

In eq. (12) of the text, the exchange correlation potential was taken as (with $N = 1$):

$$v_{xc} = -v_{J0} = -\int \frac{\rho_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (\text{A23})$$

Rearranging eq. (A22) with the help of eqs. (A13) and (A23) gives:

$$\left\langle \frac{(\rho - \rho_0)(\rho - \rho_0)}{r_{12}} \right\rangle \leq 0 \quad (\text{A24})$$

The only possible solution of above inequality is $\rho_0 = \rho$.

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